

Ch12 Chemical Kinetics

①

To be useful Rxns must occur @ a Reasonable Rate

Spontaneous does not mean fast, Just that it will happen

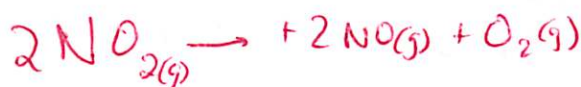


Thermodynamically
Likely But

Can exist together
Indefinitely.

Stoichiometry + Thermodynam. are not enough to know
we must understand the factors that govern the Rate of Rxn.

Reaction Rates



See table 12.1 $[\text{NO}_2] \downarrow$ while $[\text{NO}] + [\text{O}_2] \uparrow$

$$\text{Rate} = \frac{\text{Change } []}{\Delta t} = \frac{[A]_2 - [A]_1}{t_2 - t_1} = - \frac{\Delta[A]}{\Delta t} = \text{Rate}$$

↑ Avg Rate
(-) b/c disappearing
So make (-) b/c work w/ + Rate

Table 12.2 shows Average Rates for Rxn over 50s intervals

↳ Rates decrease? why?

Rates can be given for a specific time pt.

Instantaneous Rates.

↳ Pick P_{on} Avg Rate curve (12.1)

and draw a line that's tangent to it.

$$\text{Slope of tangent line} = \frac{\Delta y}{\Delta x} = \frac{\Delta [\text{NO}_2]}{\Delta t} \Rightarrow - \frac{\Delta [\text{NO}_2]}{\Delta t}$$

$$- \left(\frac{-0.0026 \text{ M}}{110 \text{ s}} \right) = 2.4 \times 10^{-5} \frac{\text{M}}{\text{s}}$$

Rates can be determined by appearance of ^{products} ~~Reactants~~ too.
But you must take into account coefficients + stoich

$$\text{Rate } -\Delta [\text{NO}_2] = \text{Rate } \Delta [\text{NO}]$$

Both same coeff → graphs are inverted forms of each other

For O₂ its appearance rate is $\frac{1}{2}$ as fast as NO₂

$$\text{Rate} = - \frac{\Delta [\text{NO}_2]}{\Delta t} = \frac{\Delta [\text{NO}]}{\Delta t} = \frac{1}{2} \frac{\Delta [\text{O}_2]}{\Delta t}$$

Same for instantaneous Rates @ given time pt.
See t = 250s on graph 1

12.2 Rate Laws Before we study Rates must make important assumption.

2

1. Reverse Rxns are not considered/Negligible b/c Rate is calculated so early. that products have not built up enough to affect React. (only look @ Reactants)
2. Must be determined by experiment!



$$\text{Rate} \propto [\text{NO}_2]$$

$$\text{Rate} = k [\text{NO}_2]^n \leftarrow \text{order} \text{ (can be 0, integer, fraction)}$$

\uparrow
Rate const

~~Rate Laws~~

~~Rate Laws~~ $\text{Rate} = -\frac{\Delta[\text{NO}_2]}{\Delta t} = k [\text{NO}_2]^n$

~~Rate Laws~~ $\text{Rate} = -\frac{\Delta[\text{NO}_2]}{\Delta t}$

\uparrow
Rate that expresses how the Rate depends on [] is Differential Rate Law
or just Rate Law

Integrated Rate Law = Explains how []'s are affected by time

Integrated & Differential are related so if you know one you know the other. Choice depends on types of data collected.

Rates are important b/c give insight into mechanism.

12.3 Determining Rate Law

Use Differential if we can measure Rate Δ compared to $[]$ Δ

Integral if we can measure $[]$ vs time t

How do we get a rate law?

1st we must find the order (power which we raise Reactant)



use differential

@ Fig 12.3

	$[\text{N}_2\text{O}_5]$
1	0.90M
2	0.45M

Rate
 $5.4 \times 10^{-4} \frac{\text{M}}{\text{s}}$

$2.7 \times 10^{-4} \frac{\text{M}}{\text{s}}$

$$\text{Rate} = - \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = k [\text{N}_2\text{O}_5]^n$$

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{k [\text{N}_2\text{O}_5]^n}{k [\text{N}_2\text{O}_5]^n} \Rightarrow \frac{5.4 \times 10^{-4} \frac{\text{M}}{\text{s}}}{2.7 \times 10^{-4} \frac{\text{M}}{\text{s}}} = \frac{[0.90\text{M}]^n}{[0.45\text{M}]^n} = 2 = 2^n$$

$n=1$

1st order when $[]$ halved the rate is halved so rate depends on power of 1.

Method of Initial Rates

↳ Initial Rate is measured just after $t=0$

Several trials @ several initial $[]$ done to determine Rate law



$$\text{Rate} = - \frac{[\text{NH}_4^+]}{\Delta t} = k [\text{NH}_4^+]^n [\text{NO}_2^-]^m$$

Compare 2 experiments

Solve for n use exp 2 + 3

$$\frac{\text{Rate 3}}{\text{Rate 2}} = \frac{k [\text{NH}_4^+]^n [\text{NO}_2^-]^m}{k [\text{NH}_4^+]^n [\text{NO}_2^-]^m} \Rightarrow \frac{5.40 \times 10^{-7} \frac{\text{M}}{\text{s}}}{2.70 \times 10^{-7} \frac{\text{M}}{\text{s}}} = \frac{k [0.20\text{M}]^n [0.010\text{M}]^m}{k [0.10\text{M}]^n [0.010\text{M}]^m}$$

$$2 = [2]^n \Rightarrow n=1$$

do similar calc get $m=1$

$$\text{Thus Rate} = k [\text{NH}_4^+] [\text{NO}_2^-] \quad \begin{array}{l} \text{1st order for each} \\ \text{2nd order overall} \end{array}$$

Plug in this solve for k

$$1.35 \times 10^{-7} \frac{\text{M}}{\text{s}} = k (0.100\text{M}) (0.0050\text{M})$$

$$k = 2.7 \times 10^{-4} \frac{1}{\text{M}\cdot\text{s}} \leftarrow \text{units will vary}$$

12.4 Integrated Rate Law

↳ Rates as a function of time.

1st look @ single reactant



$$\text{Rate} = - \frac{\Delta[A]}{\Delta t} = k[A]^n$$

we will look @ 3 cases $n = 0, 1, 2$

1st order Rxns



$$\text{Rate} = - \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = k\text{N}_2\text{O}_5$$

If we integrate (Magic)
~~natural log~~ is taken get

$$\ln [A] = -kt + \ln [A]_0$$

\uparrow \uparrow \uparrow
[] @ t Rate const initial []

Thus for $aA \rightarrow \text{Prod}$

$$\text{Rate} = - \frac{\Delta[A]}{\Delta t} = k[A]$$

Differential

$$\ln[A] = -kt + \ln[A]_0$$

Integrated

See Fig 12.4 for graph

$$\ln [N_2O_5] = -kt + \ln [N_2O_5]_0$$

$$y = mx + b$$

Integrated Eqn Shows

1. Shows $[A]$ is time dependent if $[A]_0$ + k are known any $[A]$ can be found

2. Graph shows $y = mx + b$ relation
Give STRAIGHT LINE Graph indicator of 1st order!

3. Can be expressed Ratio

$$\ln \frac{[A]_0}{[A]} = kt$$

Problem calc $[N_2O_5]^{150s}$ after Rxn starts

$$\ln [N_2O_5] = -kt + \ln [N_2O_5]_0$$

↑
find out
slope = $6.93 \times 10^{-3} s^{-1}$

$$-6.93 \times 10^{-3} s^{-1} (150s) + \ln [0.1000 M]$$

$$[N_2O_5] = 0.0353 M$$

Not Aug

Half Life for 1st Order Rxn

time for Reactant to Reach $\frac{1}{2}$ of original $[]$

$t_{\frac{1}{2}}$ Can see graphically Fig 12.5

or use integrated Rate law

$$\ln\left(\frac{[A_0]}{[A]}\right) = k t$$

$$@ t_{\frac{1}{2}} [A] = \frac{[A_0]}{2} \quad \text{thus} \quad \ln \frac{\cancel{[A_0]}}{\frac{\cancel{[A_0]}}{2}} = k t_{\frac{1}{2}}$$

$$\ln 2 = k t_{\frac{1}{2}}$$

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

Problem 12.4

2nd Order Rate Laws



$$\text{Rate} = -\frac{[A]}{\Delta t} = k[A]^2$$

Integrated 2nd order Rate Law

$$\boxed{\frac{1}{[A]} = kt + \frac{1}{[A]_0}}$$

Through
the magic of
calculus! ?

Notes 1. Plot of $\frac{1}{[A]}$ vs t yield straight line \uparrow w/slope = k

2 Can find $[A]$ if k + $[A]_0$ are known

$$\text{For } \frac{1}{2} \text{ life} \rightarrow [A] = \frac{[A]_0}{2}$$

$$\text{Thus } \frac{1}{\frac{[A]_0}{2}} = kt_{\frac{1}{2}} + \frac{1}{[A]_0}$$

$$\frac{2}{[A]_0} = kt_{\frac{1}{2}} + \frac{1}{[A]_0}$$

$$\frac{1}{[A]_0} = kt_{\frac{1}{2}} \rightarrow \boxed{t_{\frac{1}{2}} = \frac{1}{[A]_0 k}}$$

Problem Buta diene reacts to form a dimer



See slide # 9

Make sure to not e $\frac{1}{2}$ life comparisons

1st order

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

2nd

$$t_{\frac{1}{2}} = \frac{1}{k[A]_0}$$

↑

for 2nd order

each successive $\frac{1}{2}$ life is

2X the preceding

B/c $\frac{1}{2} [A]_0$ doubles $t_{\frac{1}{2}}$

0 order Rate Law

$$\text{Rate} = k [A]^0 = k \quad \text{so Rate is const}$$

integrated Rate law for 0 order

$$[A] = -kt + [A]_0 \quad \leftarrow \text{gives Straight} \\ \text{— slope}$$

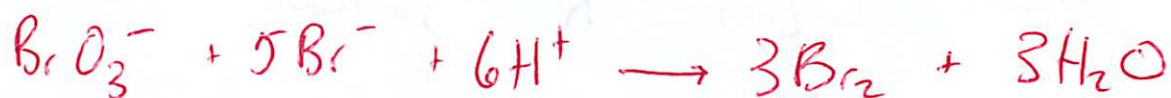
$$\text{for } t_{\frac{1}{2}} \quad \frac{[A]_0}{2} = -k t_{\frac{1}{2}} + [A]_0$$

$$t_{\frac{1}{2}} = \frac{[A]_0}{2k}$$

(Book has
typo!)

Typically these occur where Rxn takes place
on substrate. so when substrate full no
more Rxn takes place.

Integrated for Multi Reactant



$$\text{Rate} = k [\text{BrO}_3^-] [\text{Br}^-] [\text{H}^+]^2$$

Suppose $[\text{BrO}_3^-]_0 = 1 \times 10^{-3} \text{M}$ $\underbrace{[\text{Br}^-]_0 = 1.0 \text{M} \quad [\text{H}^+]_0 = 1.0 \text{M}}_{\text{[high]s so } [\text{Br}^-]_t = [\text{Br}^-]_0 \text{ \& } [\text{H}^+]_t = [\text{H}^+]_0}$
B/c they will change little

$$\text{Rate} = k [\text{Br}^-]_0 [\text{H}^+]_0^2 [\text{BrO}_3^-] = k' [\text{BrO}_3^-]$$

$$\text{thus } k' = k [\text{Br}^-]_0 [\text{H}^+]_0^2$$

$$\text{Rate} = k' [\text{BrO}_3^-] \quad \text{is 1}^{\text{st}} \text{ order}$$

Called pseudo-first order. will give same plot
and we can find k'

$$\text{so } k = \frac{k'}{[\text{Br}^-]_0 [\text{H}^+]_0^2}$$

It can work
But very
complicated

Make sure kids Read 12.5 Summary

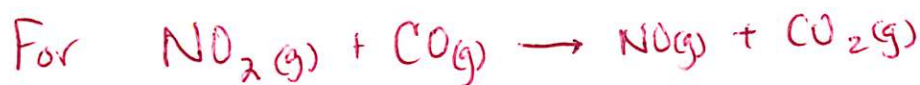
12.6 Rxn Mechanisms

7

↳ Must be experimentally derived.

↳ Chemical Rxns occur by a series of steps.

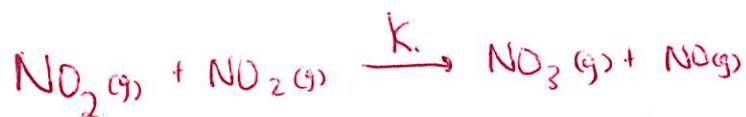
↳ Mechanisms are important to understand how a Rxn proceeds



$$\text{Rate} = k[\text{NO}_2]^2$$

But Eqn gives no mention of Rxn mechanism

Mech is thought to involve the following steps



k_1, k_2 rate constants for each step

NO_3 is an intermediate - species formed + consumed in Rxn
Not Reactant or Product.

Elementary Steps - a Rxn whose Rate law

↓
Process occur in single events
Elementary Rxn

* Can be written from its
Molecularity (so Rate expression is the Rxn)

Molecularity - # of Species that must collide
to produce the Rxn indicated in
that Step.

See table 12.7 unimolecular, bi. molecular, termolecular

So when $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$ \rightarrow Bimolecular elementary step
Rate B/c Prob of all of things colliding

~~Rxn~~ Mechanism is series of elementary steps that

1. Sum of steps give overall Rxn
2. Mech must agree w/ Rate Law



← Meet Req #1

2nd Req depends on Rate Determining Step

8

↳ Step that is slow and determines how fast Rxn proceeds.



Rate laws can be written from RDS directly.

$$\text{Rate} = \frac{\Delta[\text{NO}_3]}{\Delta t} = k_1[\text{NO}_2]^2$$

↳ B/c it depends on NO_2 colliding! 2 are needed to collide thus $\text{Rate} \propto [\text{NO}_2]^2$

Overall Rate = $k_1[\text{NO}_2]^2$ b/c Rate cannot be faster than slowest step

How is mech made?

1st get Rate Law

2nd use 2 rules of Rxn Mechanism to deduce mechanisms

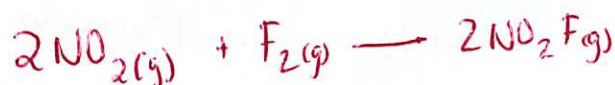
3rd Experiment + try to prove them correct.
Cannot absolutely date only possible

we can't see molecules touch!

Ex 12.6

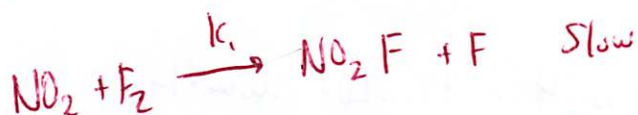
pg 551

Q10



$$\text{Rate law} = k[\text{NO}_2][\text{F}_2]$$

Suggested Mech

yes it is possible

other mechs may exist



Model for Chemical Kinetics

9

Rate of Rxn affected by $[T]$'s \rightarrow Rate Law

Temperature food spoils slow @ low T

~~Molecules~~ Molecules must Collide to React!

Collision Theory

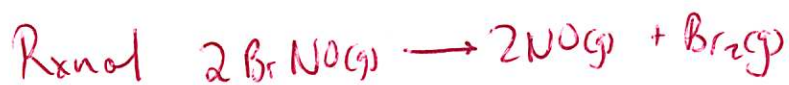
More molecules more collisions

Higher T more KE more ~~from~~ collisions

(Rate constant \uparrow w/ T)

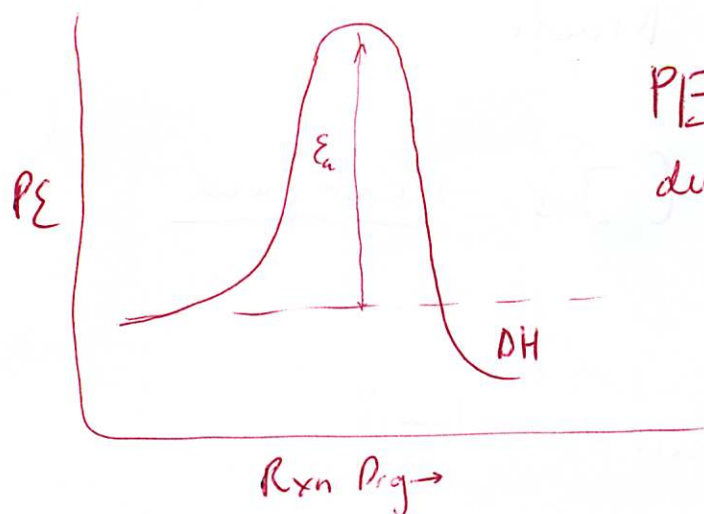
However Rate of Rxn is smaller than collision freq why?

Activating Energy must be overcome to produce a Rxn. - Activation E (E_a)
It's a threshold.



E_a comes from KE of molecules b/f collision

Fig 12.11



PE comes from KE during collision

Rate not dependent on DH but size of E_a

E is Req'd to get over hill E B/w to molecules w/
Small KE is not enough to meet E_a so higher T gives
more E to meet that.

Fig 12.12 T₂ has higher T so more collisions are @ a higher E

Fraction of collisions ↑ exponentially w/ T

Arrhenius thought that

$$\text{# of effective collisions} = \text{total collisions} \left(e^{-E_a/RT} \right)^{\text{only}}$$

however even though enough E is present not in correct orientation

Molecular orientations must be aligned correctly.

10

So 2 things needed E_a + Orientation.

$$\text{Thus } k = A e^{-E_a/RT}$$

↑
Frequency factor - ~~to~~ consider ~~that~~ collisions ~~of~~ which
collisions have proper orientation

take nat log get

$$\ln(k) = \frac{-E_a}{R} \left(\frac{1}{T} \right) + \ln(A)$$

$$y = m x + b$$

Fig 12.14 Can graph Eqn to find E_a by
finding k @ diff T 's and plotting vs $\frac{1}{T}$

$$\text{Find slope} = \frac{-E_a}{R}$$

or can find E_a

$$\ln(k_1) = -\frac{E_a}{RT_1} + \ln(A) \quad \ln(k_2) = -\frac{E_a}{RT_2} + \ln(A)$$

Combining Eqs b/c $\ln A$

$$\ln(k_2) = -\frac{E_a}{RT_2} + \left(\ln(k_1) + \frac{E_a}{RT_1} \right)$$

$$\ln(k_2) - \ln(k_1) = -\frac{E_a}{RT_2} + \frac{E_a}{RT_1}$$

$$\ln \frac{k_2}{k_1} = +\frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Lehrer Chem Chap 8

P537 # 12.8

12.8 Catalysis - speeds R_{rxn} by lower E_a w/o being consumed

Enzyme - Biological catalysts

2 Types heterogeneous - diff phase

homogeneous - same phase

Heterogeneous Catalysts

11

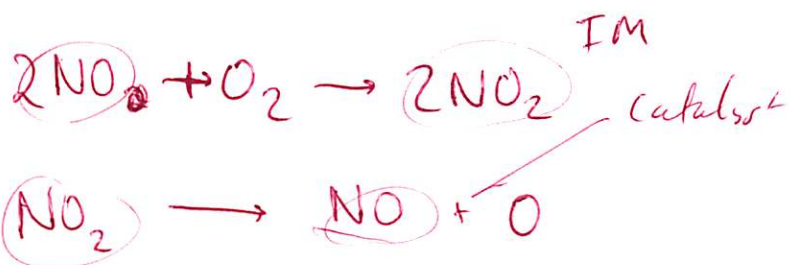
↳ gas on to solid - adsorption - collection of one substance
Surface of another (Bratta)

Seen w/ Hydrogenation



Homogeneous - same phase

NO toward Ozone



Upper atmos pher



Ozone depletion